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(54) Title: PHOTOVOLTAIC CELLS

## (57) Abstract

New TiO<sub>2</sub> containing photovoltaic cells effective in the conversion of visible light to electric energy as follows: a photovoltaic cell comprising: a) an electrically conductive element to which one or more titanium dioxide layers have been applied (hereinafter component a); b) a solid electrolyte (hereinafter component b); and/or c) an electrically conductive element through which light can pass to the TiO<sub>2</sub> layer (hereinafter component c).

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## PHOTOVOLTAIC CELLS

The invention relates to new TiO<sub>2</sub> containing photovoltaic cells effective in the conversion of visible light to electric energy.

According to the invention there is provided a photovoltaic cell comprising:

- a) an electrically conductive element on to which one or more titanium dioxide layers have been applied (hereinafter component a);
- b) a solid electrolyte (hereinafter component b); and/or
- c) an electrically conductive element through which light can pass to the TiO<sub>2</sub> layer (hereinafter component c).

Further according to the invention there is provided a photovoltaic cell (hereinafter the photovoltaic coaxial cell) comprising

- a) a cylindrical conductive element (eg a textile conductive filament or a wire such as copper wire) on to which one or more titanium dioxide layers have been applied (hereinafter component a<sub>1</sub>);
- b) a solid electrolyte that has been applied concentrically around the cylindrical component a<sub>1</sub> (hereinafter component b<sub>1</sub>); and/or
- c) an electrically conductive element through which light can pass to the TiO<sub>2</sub> layer, that has been applied concentrically around the cylindrical component a<sub>1</sub> (hereinafter component c<sub>1</sub>).

Preferably component a) comprises a support, (preferably a glass plate coated with metal oxide, a metal surface or a polymer sheet (preferably an intrinsically conductive polymer)) to which the TiO<sub>2</sub> layer is applied. Optionally, component a) is transparent. By the term "transparent" is meant that at least 60%, preferably 70%, more preferably at least 80%, especially 80-98% of incident light passes through the glass.

Preferably the TiO<sub>2</sub> layer comprises rutile and anatase, more preferably anatase.

Preferably the titanium dioxide is doped with a metal ion, which may be selected from a divalent or trivalent metal or boron. Preferred dopant is aluminium.

Preferably the titanium dioxide layer is a film. Preferably the film has a roughness factor greater than 20, the roughness factor being defined as the ratio of true to apparent surface area. Roughness factor is defined in USP 5,084,365 and 4,927,721. More preferably the roughness factor is 20-1000, most preferably 50-200.

Preferably the titanium dioxide layers are built up on the surface of the conductive layer of the electrically conductive elements of compound a) using one of two methods. One is the sol-gel method described in "Stalder and Augustynski in J. Electrochem. Soc. 1979, 126:2007" and in Example 1. Another is the "colloidal method" described in Examples 2 and 3.

Preferably in a photovoltaic cell or a photovoltaic coaxial cell according to the invention, a photosensitiser (preferably a photosensitizer dye) is applied onto the TiO<sub>2</sub>. Preferably such a photosensitizer is a ruthenium, osmium or iron complex or a supramolecular complex of two or three transition metals or a thin layer of iron sulphide (FeS<sub>2</sub> - pyrite).

Preferably component b) (and b<sub>1</sub>) is a charge transfer relay. The charge transfer relays present in the electrolyte transport electric charge from one electrode to the other. They act as pure mediators and undergo no chemical alteration during the operation of the cell. More preferably component b) (and b<sub>1</sub>) is a glassified solid electrolyte, preferably a precious metal salt, more preferably a silver, platinum or gold salt such as halide or borate especially silver iodide or silver borate. What is meant by a glassified solid electrolyte is a product that can be applied as a fluid that solidifies on further treatment, such as heating.

Preferably component c) (and c<sub>1</sub>) has a transparency of at least 60%, more preferably at least 80%, most preferably 80-98%.

Preferably component c) (and c<sub>1</sub>) is either

- i) an intrinsically conductive polymer based on a polymer selected from polyacetylene, poly(p-phenylene), poly(p-phenylenevinylene), poly-(p-phenylenesulphide), polypyrrole, polythiophene, polyfurane, polyazulene, polyazine (especially when polyazine it is polyazine doped with halogen eg iodine) and polyaniline; (more preferably polyaniline, polypyrrole or polyacetylene) (hereinafter component i); or
- ii) a composite or blend of a homopolymer or copolymer of an intrinsically conductive polymer based on a polymer selected from polyacetylene, poly(p-phenylene), poly(p-phenylene vinylene), poly(p-phenylene sulphide), polypyrrole, polythiophene, polyfurane, polyazulene, polyazine (especially when polyazine it is polyazine doped with halogen eg iodine) and polyaniline; (more preferably polyaniline, polypyrrole or polyacetylene) with up to 60% of a polymer selected from polyamide, polyolefins (polyethylene or polypropylene), polycarbonate and polymethacrylate (hereinafter

component ii) or

iii) polyacrylate and copolymers preferably doped with metallic oxides, preferably with SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and/or ZnO (hereinafter component iii); or

a mixture of components i, ii and/or iii.

Preferably component c) (and c<sub>1</sub>) is selected from commercially available electrically conductive polymeric products such as Lutamer P 160 from BASF which is a polymer based on polypyrrole or ICP 275 based on polyaniline from Zipperling or Almeaco Protect from Henkel or Covexal from Cowa in Singen (FRG) which is a polyacrylate and copolymer doped with ZnO (and optionally SnO<sub>2</sub>) can also be used. Such polymers are described in the article "Tapping the power of intrinsic conductivity" A. Stuart Wood in Modern Plastics August 1991, the contents of which is incorporated herein by reference.

The components a) and c) (and a<sub>1</sub> and c<sub>1</sub>, respectively) may be further doped with halogen e.g. iodine, preferably in an amount of not more than 10%, preferably 2-5% by weight of the component.

Preferably component c) when not an intrinsically conductive polymer used in a photovoltaic cell according to the invention is made of tin dioxide doped with ca.0.8 atom percent of fluorine and this layer is deposited on a transparent substrate made of low-cost soda lime float glass. This type of conducting glass can be obtained from Asahi Glass Company, Ltd. Tokyo, Japan. under the brand name of TCO glass. The transparent conductive layer can also be made of indium oxide doped with up to 5% tin oxide, deposited on a glass substrate. This is available from Balzers under the brand name of ITO glass.

Further according to the invention a photovoltaic cell comprises

- a) an electrically conductive element (hereinafter the first electrode);
- b) optionally (though preferably) a solid (preferably glassified) electrolyte preferably based on a precious metal salt (eg silver, gold or platinum halide (eg iodide or bromide)) and
- c) an intrinsically conductive polymer (herein defined as the second electrode) (with no TiO<sub>2</sub> coating) which contacts the TiO<sub>2</sub> layer of the first electrode (or the electrolyte if present), whereby there is visible light transmittance through at least the first or second electrode of at least 60%; (preferably also solar light transmittance is at least 60%).

Preferably the first electrode is a metal, polymer or glass plate substrate to which an electrically conductive surface has been applied, to which one or more layers (preferably a film of 0.1-50 microns) of titanium dioxide has been applied; (preferably the TiO<sub>2</sub> is coated with a photosensitizer - preferably a transition metal compound e.g. dyestuff).

Preferably both electrodes have a surface resistance of 5-1000 ohm/cms<sup>2</sup>, more preferably 5-100 ohm/cms<sup>2</sup>, most preferably 5-15 ohm/cms<sup>2</sup>, especially 10 ohm/cms<sup>2</sup>.

Preferably the intrinsically conductive polymers are selected from components i) and ii) defined above.

The second electrode (also known as "the counterelectrode") may be coated with a thin layer (preferably up to 10 microns thickness) of an electrocatalyst. The role

of the electrocatalyst is to facilitate the transfer of electrons from the counterelectrode to the electrolyte.

A further possible modification is to make one of the electrodes reflect light so that light having passed through the other electrode is reflected back into the cell, from the said one electrode.

The first electrode may be supported on a glass, metal or polymer substrate (which polymer may also be selected from those polymers that can be used for component c)).

Optionally (though preferably) the second electrode is such that the substrate preferably has a visible light transmittance of 60-99%, more preferably 85-95%. Preferably the second electrode has a surface resistance of less than 10 ohms per square cm.

Preferably the first electrode is glass coated with a film of metal oxide, preferably tin oxide (e.g. ITO glass from Fa. Balzars).

Photovoltaic cells according to the invention have advantages selected from the following:

1. Where solid electrolyte is present, the use of fluid electrolyte is avoided. This brings a good long term light fastness and avoids the drawback associated with cells having fluid electrolyte of deterioration of the first electrode and avoids deterioration of the electrodes of the integrated cells.
2. A photovoltaic cell according to the present invention provides a better overall stability from systems previously known.
3. With this system, it will be possible to build very thin and flexible solar cells

that could be adapted easily to any form.

4. The photovoltaic coaxial cell may also have the following advantages:

- a) the cell will be automatically integrated by a simple and periodic isolation of the wires;
- b) the cell avoids the need for conductive wire on the surface of the cell between the modules thereby making it cheaper to make;
- c) the cell can be produced continuously (eg in a fashion similar to that described in EP 294, 504; for example by passing a cylindrical conducting element through a titanium dioxide colloid or paste followed by drying and sintering at 450°C. This is followed by optionally (though preferably) dipping the element into a photosensitizer solution followed by drying. The coated element is then passed through molten electrolyte (at elevated temeprature) which is then solidified on the element by cooling. Electrically conductive polymer is brought into molten state and the coated element is passed conventionally there through and the polymer is cooled to solidify the polymer on the element. In order to increase the voltage "gridding" is carried out conventionally);
- d) there is increased use for the cell due to its adaptability to any surface;
- e) it may be a more efficient cell; and
- f) it may have improved heat dissipation.

For producing the electrically conductive element or first electrode with TiO<sub>2</sub> applied by the sol gel method it is preferable that the titanium dioxide is doped with a divalent or trivalent metal in an amount of not more than 15% doping by weight based on the amount of TiO<sub>2</sub> present. However, the deposition of the pure dopant in the form of a very thin top oxide layer can also be advantageous. A blocking layer is formed which impedes leakage current at the electrically conductive element-electrolyte junction. TiO<sub>2</sub> film can be formed by the sol gel

process method described in Example 1. Preferably the total thickness of the TiO<sub>2</sub> film is from 5 to 50 microns (more preferably 10-20 microns).

The photosensitising layer may be produced by applying to the TiO<sub>2</sub> layer a dye according to the invention defined for example in WO 91/ 16719 (=PCT/EP 91/00734) (Graetzel) the content of which is incorporated herein by reference. Especially incorporated herein by reference are the dyes set out in WO 91/16719.

The invention will now be illustrated by the following Examples.

In the Figures that follow, where elements are the same in each Figure the same numbering is used. The number (2) for example in Figures 1-4 refers to the same element, i.e. the photosensitizer dye.

Light photon in each Figure are referred to as 9.

**Example 1**

A preferred photovoltaic cell is shown in Figure 1..

The photovoltaic cell is based on the sensitization of an aluminium doped titanium dioxide film supported on conducting glass and can be fabricated as follows:

A stock solution of organic titanium dioxide precursor is prepared by dissolving 21 mmols of freshly distilled  $TiCl_4$  in 10 mL of absolute ethanol.  $TiCl_4$  in the ethanol solution gives titanium alkoxide spontaneously which hydrolyses to give  $TiO_2$ . The stock solution is then diluted further with absolute ethanol to give two solutions (solution A and solution B) having titanium contents of 25 mg/ml (solution A) and 50 mg/ml (solution B). A third solution (solution C) is prepared from solution B by the addition of  $AlCl_3$  to yield an aluminium content of 1.25 mg/ml. A conducting glass sheet from Asahi Inc. Japan having a surface area of 10  $cm^2$  and having a visible transmittance of at least 85% and a surface resistance smaller than 10 ohms per square cm is used as the support on to which to which the  $TiO_2$  can be deposited as a layer. Prior to deposition, the glass is cleaned with alcohol. A droplet of solution A is spread by use of a doctor blade over the surface of the conducting glass to produce a thin coating. Subsequently the layer is hydrolysed at 28°C for 30 minutes in a special chamber where the humidity is kept at 48% of the equilibrium saturation pressure of water. Thereafter the electrode is heated in air in a tubular oven kept at 450°C, preheating it in the entrance of the oven for 5 minutes followed by 15 minutes of heating in the interior. Three more layers are produced in the same way. Subsequently, 5 thicker layers are deposited by using solution B. The same procedure as for the first layers is applied.

Finally solution C is used to deposit the last two layers containing the aluminium dopant. The heating of the last layer in the tubular oven is extended from 15 to 30 minutes. The total thickness of the titanium dioxide film is between 10 and 20 microns.

Prior to deposition of the dye, the film is subjected to a sintering treatment in highly purified argon (99.97%). A horizontal tubular oven is employed. After insertion of the glass sheet with the TiO<sub>2</sub> film, the film is twice purged with argon. The glass sheet is then heated under argon flux at a flow rate of 2.5L/h and a temperature gradient of 500°C/h up to 550°C at which temperature it is maintained for 35 minutes. This treatment produces a crystal modification of TiO<sub>2</sub>, that is an anatase film with a surface roughness factor of 80-200.

After cooling under a continuous flow of argon, the glass sheet is immediately transferred to an alcoholic solution a chromophore, the chromophore employed being the trimeric ruthenium complex



where L is 2,2'bipyridyl-4,4'-dicarboxylic acid and L' is 2,2'-bipyridyl. Its concentration in absolute alcohol is 5X10<sup>-4</sup>M. Prolonged exposure of the film to the open air prior to dye absorption is avoided in order to prevent hydroxylation of the TiO<sub>2</sub> surface as the presence of hydroxy groups at the electrode surface interferes with the dye uptake. The adsorption of chromophore from the ethanolic solution is allowed to continue for 30 minutes after which time the glass sheet is withdrawn and washed briefly with absolute ethanol. The TiO<sub>2</sub> layer on the sheet assumes a deep red colour because of the chromophore coating.

A photovoltaic cell according to the invention is shown in Figure 1. It is

constructed, using a dye (2) coated on a TiO<sub>2</sub> film (3) supported on an Asahi conducting glass as described above support (4+5) this forming the working electrode (2-5). This is supported on a transparent conductive tin dioxide layer (4) and a glass substrate (5) as a photoanode. The cell has a sandwich-like configuration, the working electrode (2-5) being directly in contact with the counterelectrode, a transparent polymer (1) (an intrinsically conductive polymer - ICP 275 available from Zipperling or Lutamer P 160 available from BASF) of a thickness of ca. 20 microns.

A transparent glass (or ICP transparent polymer) working electrode is an advantage for photovoltaic applications since it allows the harvesting of light from both sides. Alternatively, the working electrode can contain a reflective surface.

Alternatively, a modification to the cell of Figure 1 is shown in Figure 2. This differs from Figure 1 by the presence of a solid state electrolyte (6), which is a thin (20 microns) layer of silver iodide, located between the working electrode (2-5) and the counter electrode (1).

### **Example 2**

A transparent TiO<sub>2</sub> film from colloidal titanium dioxide particles is deposited on an alumina (or conducting glass) support (5) and sintered to yield a coherent highly porous semiconducting film that is transparent and can be used instead of the TiO<sub>2</sub> layer film in Example 1. This is made as follows:

Colloidal titanium oxide particle of approximately 10nm are prepared by hydrolysis of titanium isopropoxide as follows:

125 ml of titanium isopropoxide is added to a solution of 0.1M nitric acid in 750ml of water whilst stirring. A precipitate of amorphous titanium dioxide is formed under these conditions. This is heated to 80°C for approximately 8 hours, stirring vigorously, resulting in peptisation of the precipitate and formation of a clear solution of colloidal anatase. The anatase structure of the titanium dioxide particles is established by Raman spectroscopy. The sol is concentrated by evaporation of the solvent in vacuum at room temperature until a viscous liquid is obtained containing the colloidal particles. At this stage the nonionic surfactant TRITON X-100 (commercially available from Rohm & Hass) in any amount of 40% weight of TiO<sub>2</sub> is added to reduce cracking of the film when applied to a substrate.

The titanium dioxide films are formed by spin coating the concentrated sol on to a conducting glass substrate. Usually it is sufficient to apply 6 to 10 layers in order to obtain semiconductor membranes of sufficient surface area to give excellent visible light harvesting efficiencies after deposition of a monolayer of the sensitizer.

A three layer structure is formed, the lowest being the glass support followed by the 0.5 micron thick fluorine-doped SnO<sub>2</sub> (the fluorine dopant is less than 5%) and the 2.7 micron thick titanium dioxide layer. It would appear to be a TiO<sub>2</sub> film composed of a three dimensional network of interconnected particles having an average size of approximately 16nm. Apparently, significant particle growth occurs during sintering.

The transparent TiO<sub>2</sub> films are tested in conjunction with a sensitizer, Ru L<sub>3</sub> where L is 2,2'bipyridyl-4,4'dicarboxylic acid regenerative cell for the generation of electricity from visible light. The results can be represented where the photocurrent under simulated sunlight (intensity ca 30W/m<sup>2</sup>) is plotted as a

function of cell voltage.

A copolymer based on 70% polyamide and 30% polyaniline is melted at 300°C and is applied by a squeegee (or doctor blade) spreading a sheet of polymer over the ruthenium complex surface to a thickness of 20 microns.

### **Example 3**

A sheet of plastics (Lutamer P160 - BASF - a polypyrrole polymer) having a size of 2x9.6 cm<sup>2</sup> is coated with a colloidal titanium dioxide film according to the procedure of Example 2. A total of 7 layers of TiO<sub>2</sub> colloid are deposited successively by spin coating and the film is subjected each time to a temperature of 200°C for 30 minutes. 30% (w/w) of TRITON X 405 surfactant is added in order to avoid cracking of the film.

The final thickness of the titanium dioxide film is 5 microns.

Immediately before coating with dyestuff, the film is fired for 1 hour at 250°C. The coating of TiO<sub>2</sub> with dyestuff is performed by immersing the plastics sheet for 16 hours in an ethanolic solution containing the trimeric ruthenium complex RuL<sub>2</sub>(CNRuL'CN)<sub>2</sub> where L stand for 2,2-bipyridyl 4,4'-dicarboxylate and L' stands for 2,2'-bipyridyl. After coating, the plastics sheet displays an intensive dark red coloration. Due to the high concentration of dyestuff, the porous film is capable of harvesting photons over a very broad spectral range extending from 400 to 750 nm.

After dye deposition, the plastics sheet is cut into two parts each having a size of ca 9 cm<sup>2</sup>. These sheets serve as working electrodes (photo-anodes) in the module whose assembly is described further below.

Transparent counterelectrodes are made of the same type of polymer as the working electrodes, except the counterelectrode is not coated with TiO<sub>2</sub>.

#### Example 4

A photovoltaic cell which is a modification of the cell of Figure I, as shown in Figure 3 and can be made up as described in Example 1 in which the counter electrode and the working electrode are the same. The working electrode comprises titanium dioxide layer 3 to which dye 2 has been applied, supported on an Asahi conducting glass support (4+5) comprising a transparent conductive tin dioxide layer (4) and a glass substrate (5). The counter electrode is an Asahi conducting glass support (7 and 8) comprising a transparent conductive tin dioxide layer (7) and a glass substrate (8). These glass supports are made according to the method of Example 1. A solid electrolyte (6) of 20 microns separates the working electrode (4,5) from the counterelectrode (7,8).

#### Example 5

A further embodiment of a photovoltaic cell according to the invention can be seen in Figure 4, in which a conductive wire such as copper (11) supports a layer of TiO<sub>2</sub> (13) coated with dyestuff (12) on its outer surface and surrounded by a intrinsically conductive polymer (ICP 275 or Lutamer P 160 of Example 1) (14) as the counterelectrode.

The wire can be coated with TiO<sub>2</sub> by a method as described in Example III of EP 294 504 by drawing it though a solution of TiO<sub>2</sub>, as described in Example 1 of EP 294 504. Coating with dyestuff is carried out by drawing the TiO<sub>2</sub> coated wire through a dyestuff solution (of the dye of Example 1 of the present application). Coating with an intrinsically conductive polymer is carried out by drawing the

wire through a melt of the polymer. The amount of chemical taken up can be regulated by the rate of drawing the wire through the appropriate solution and the temperature of the solution.

The complexes of the other compounds of Examples 1 to 33 of PCT/EP91/ 00734 can be used in place of the ruthenium complexes of Examples 1 to 5 in the photovoltaic cell. These components are shown in Figure 1 below.

**Table 1**

Photo. Compd	Complex	L	L'
1	[Ru(L <sub>2</sub> ((CN) <sub>2</sub> Ru(L') <sub>2</sub> ) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> bpy	2,2'-bpy
2	[Ru(L <sub>2</sub> ((CN) <sub>2</sub> Ru(L') <sub>2</sub> ) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> bpy	
3	[Ru(L <sub>2</sub> ((CN) <sub>2</sub> Ru(L') <sub>2</sub> ) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> bpy	4,4'-(Me) <sub>2</sub> bpy
4	[Ru(L <sub>2</sub> ((CN) <sub>2</sub> Ru(L') <sub>2</sub> ) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> bpy	4,4'-(ph) <sub>2</sub> bpy
5	[Ru(L <sub>2</sub> ((CN) <sub>2</sub> Os(L') <sub>2</sub> ) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> bpy	2,2'-bpy
6	RuL <sub>2</sub> (CN) <sub>2</sub>	4,4'-(COOH) <sub>2</sub> bpy	
7	RuL <sub>2</sub> (CN) <sub>2</sub>	2,2'-bpy	
8	RuL <sub>2</sub> (CN) <sub>2</sub>	4,4'-(Me) <sub>2</sub> bpy	

in which "bpy" = 2,2' - bipyridyl

"Me" = methyl

"ph" = phenyl

**Examples 9-33 of PCT/EP 91/00734**

By a method analogous to that of Example 1, complexes as defined in Table 2 can be prepared from suitable reactants.

In Table 2 below, bpy = 2,2' bipyridyl; biq = 2,2' biquinoline and phen = 1,10 phenanthroline

in compounds, 19 2-phenylpyridine is used

in compound 22 straight and branched alkyl groups are used

in compound 26 N,N-tetramethyl and C,C - tetramethyl ethylene diamine are used

in compound 27 2,2' bis(diphenylphosphino)-1,1'binaphthylene is used

in compound 28, 30 and 33 1,10 orthophenanthrolene is used and

in compound 31 4-(2-pyridyl) azo resorcinol is used

Table 2

#	Complex	L	L'
9	[RuL <sub>3</sub> ]	4,4',5,5'-(COOH) <sub>4</sub> -2,2'-bpy	-
10	[RuL <sub>3</sub> ]	3,8-(COOH) <sub>2</sub> -4,7-(OH) <sub>2</sub> phen	-
11	[RuL <sub>3</sub> ]	6,6'-(COOH) <sub>2</sub> -2,2'-bpy	-
12	[RuL <sub>3</sub> ] [Ru <sup>2+</sup> , Ru <sup>3+</sup> ]	4,4'-(OMe) <sub>2</sub> -2,2'-bpy	-
13	[RuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> -2,2'-biq	-
14	[RuL <sub>2</sub> Cl <sub>2</sub> ]	4,4',5,5'-(COOH) <sub>4</sub> -2,2'-bpy	--
15	[RuL <sub>2</sub> (CN <sub>2</sub> ) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	-
16	[RuL <sub>2</sub> L'(H <sub>2</sub> O)]	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	4-(COOH)pyridine
17	[RuL <sub>2</sub> L'(H <sub>2</sub> O)]	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	3,5-(COOH) <sub>2</sub> pyridine
18	[RuL <sub>2</sub> L'(H <sub>2</sub> O)]	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	pyridine
19	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	phenylpyridine
20	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	4,4'-(COOH) <sub>2</sub> -2,2'-biq
21	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	4,4'-(phenyl) <sub>2</sub> -2,2'-bpy
22	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	C <sub>13</sub> H <sub>27</sub> -2,2'-bpy
23	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	4,4'-(Me) <sub>2</sub> -2,2'-bpy
24	[RuL <sub>2</sub> L']	2,2'-bpy	1,10-phenanthroline-5,6-dioxime

#	Complex	L	L'
25	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	1,2-bis(2-pyridyl)ethane
26	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	(Me) <sub>4</sub> -ethylenediamine
27	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	binaphthyl
28	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	3,8-(COOH) <sub>2</sub> -1,7-(OH) <sub>2</sub> phen
29	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	dimethylglyoxime
30	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	4,7-(OH) <sub>2</sub> -1,10-phen
31	[RuL <sub>2</sub> L']	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	2-azopyridylresorcinol
32	[RuL <sub>2</sub> L']	4,4'-(phenyl) <sub>2</sub> -2,2'-bpy	4,4'-(COOH) <sub>2</sub> -2,2'-bpy
33	[RuL <sub>2</sub> L']	4,4'-(phenyl) <sub>2</sub> -2,2'-bpy	4,7'-(OH) <sub>2</sub> -1,10-phen
34	[RuL'(SCN) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	2,2'-bpy
35	[RuL <sub>2</sub> (SCN) <sub>2</sub> ]	4,4'-(COOH) <sub>2</sub> -2,2'-bpy	

Claims:

1. A photovoltaic cell comprising:
  - a) an electrically conductive element to which one or more titanium dioxide layers have been applied (hereinafter component a);
  - b) a solid electrolyte (hereinafter component b); and/or
  - c) an electrically conductive element through which light can pass to the TiO<sub>2</sub> layer (hereinafter component c).
2. A photovoltaic cell (hereinafter the photovoltaic coaxial cell) comprising
  - a) a cylindrical conductive element (eg a textile conductive filament or a wire such as copper wire) on to which one or more titanium dioxide layers have been applied (hereinafter component a<sub>1</sub>);
  - b) a solid electrolyte that has been applied concentrically around the cylindrical component a<sub>1</sub> (hereinafter component b<sub>1</sub>); and/or
  - c) a light transmitting electrically conductive polymer, through which light can pass to the TiO<sub>2</sub> layer, that has been applied concentrically around the cylindrical component a<sub>1</sub> (hereinafter component c<sub>1</sub>).
3. A cell according to Claim 1 or Claim 2 in which the titanium dioxide film has a roughness factor greater than 20, the roughness factor being defined as the ratio of true to apparent surface area.
4. A cell according to any one of the preceding claims in which a photosensitiser is applied to the TiO<sub>2</sub> layer.

5. A cell according to any one of the preceding claims in which component  
b) is a glassified solid electrolyte
6. A cell according to any one of the preceding claims in which component  
c) is either
  - i) an intrinsically conductive polymer based on a polymer selected from polyacetylene, poly(p-phenylene), poly(p-phenylenevinylene), poly(p-phenylenesulphide), polypyrrole, polythiophene, polyfurane, polyazulene, polyazine and polyaniline; (hereinafter component i) or
  - ii) a composite or blend of a homopolymer or copolymer of an intrinsically conductive polymer based on a polymer selected from polyacetylene, poly(p-phenylene), poly(p-phenylenevinylene), poly(p-phenylene sulphide), polypyrrole, polythiophene, polyfurane, polyazulene, polyazine (including polyazine doped with halogen eg iodine) and polyaniline; with up to 60% of a polymer selected from polyamide, polyolefins, polycarbonate and polymethacrylate (hereinafter component ii) or
  - iii) polyacrylate and copolymers thereof (hereinafter component iii); or
- a mixture of components i, ii and/or iii.
7. A photovoltaic cell comprising
  - a) an electrically conductive element (hereinafter the first electrode);
  - b) optionally a solid electrolyte; and
  - c) an intrinsically conductive polymer (hereinafter the second electrode) (with no TiO<sub>2</sub> coating) which contacts the TiO<sub>2</sub> layer of the first electrode

(or the electrolyte if present), whereby the visible light transmittance of at least the polymer is at least 60%.

8 A cell according to Claim 7 in which the intrinsically conductive polymer is selected from components i) and ii).

- i) an intrinsically conductive polymer based on a polymer selected from polyacetylene, poly(p-phenylene), poly(p-phenylenevinylene), poly(p-phenylenesulphide), polypyrrole, polythiophene, polyfurane, polyazulene, polyazine and polyaniline; (hereinafter component i) or
  - ii) a composite or blend of a homopolymer or copolymer of an intrinsically conductive polymer based on a polymer selected from polyacetylene, poly(p-phenylene), poly(p-phenylenevinylene), poly(p-phenylene sulphide), polypyrrole, polythiophene, polyfurane, polyazulene, polyazine (including polyazine doped with halogen eg iodine) and polyaniline; with up to 60% of a polymer selected from polyamide, polyolefins, polycarbonate and polymethacrylate (hereinafter component ii).
9. A photovoltaic cell substantially as herein described with reference to any one of Examples 1 to 5.

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Figure 1

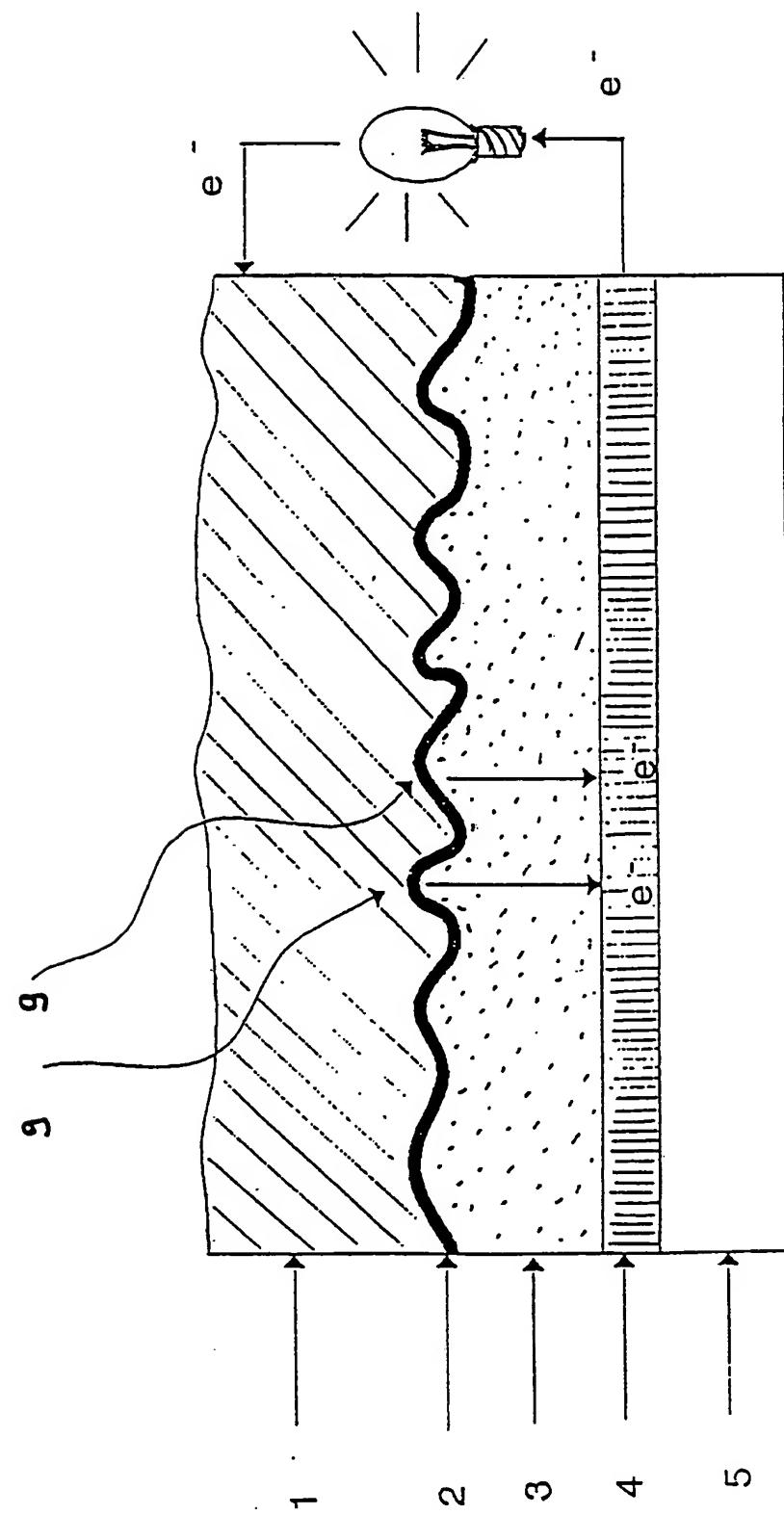
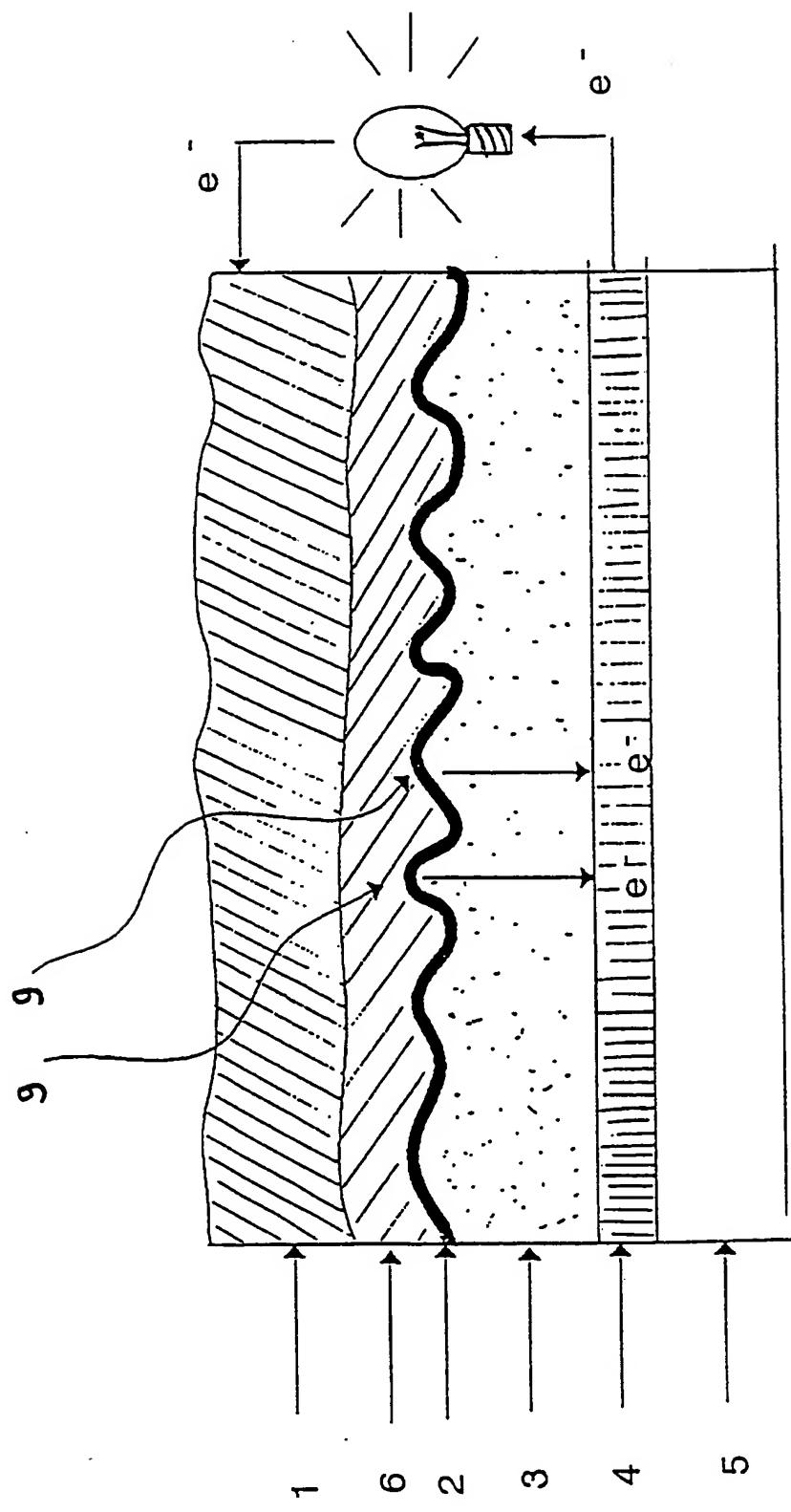


Figure 2



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Figure 3

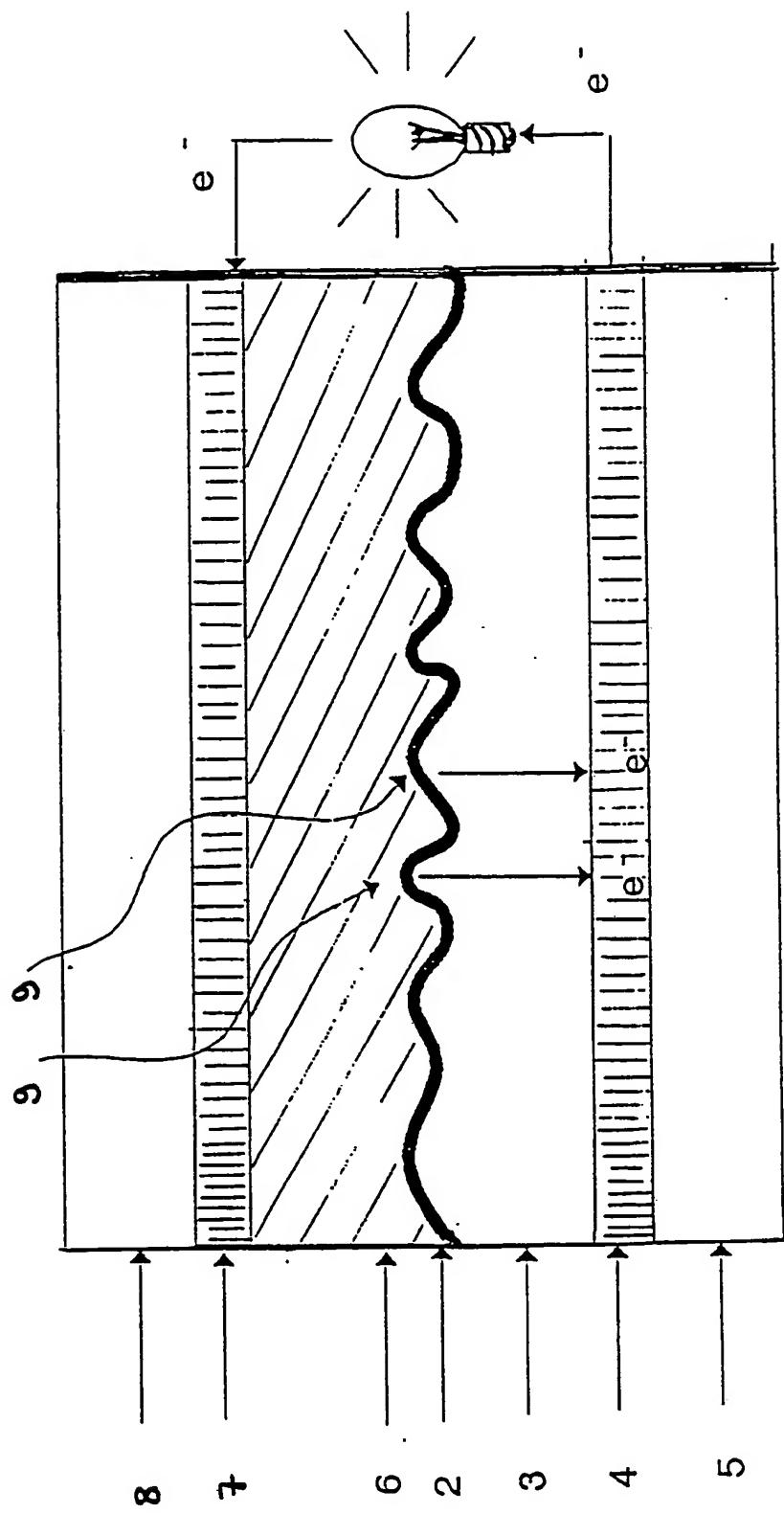
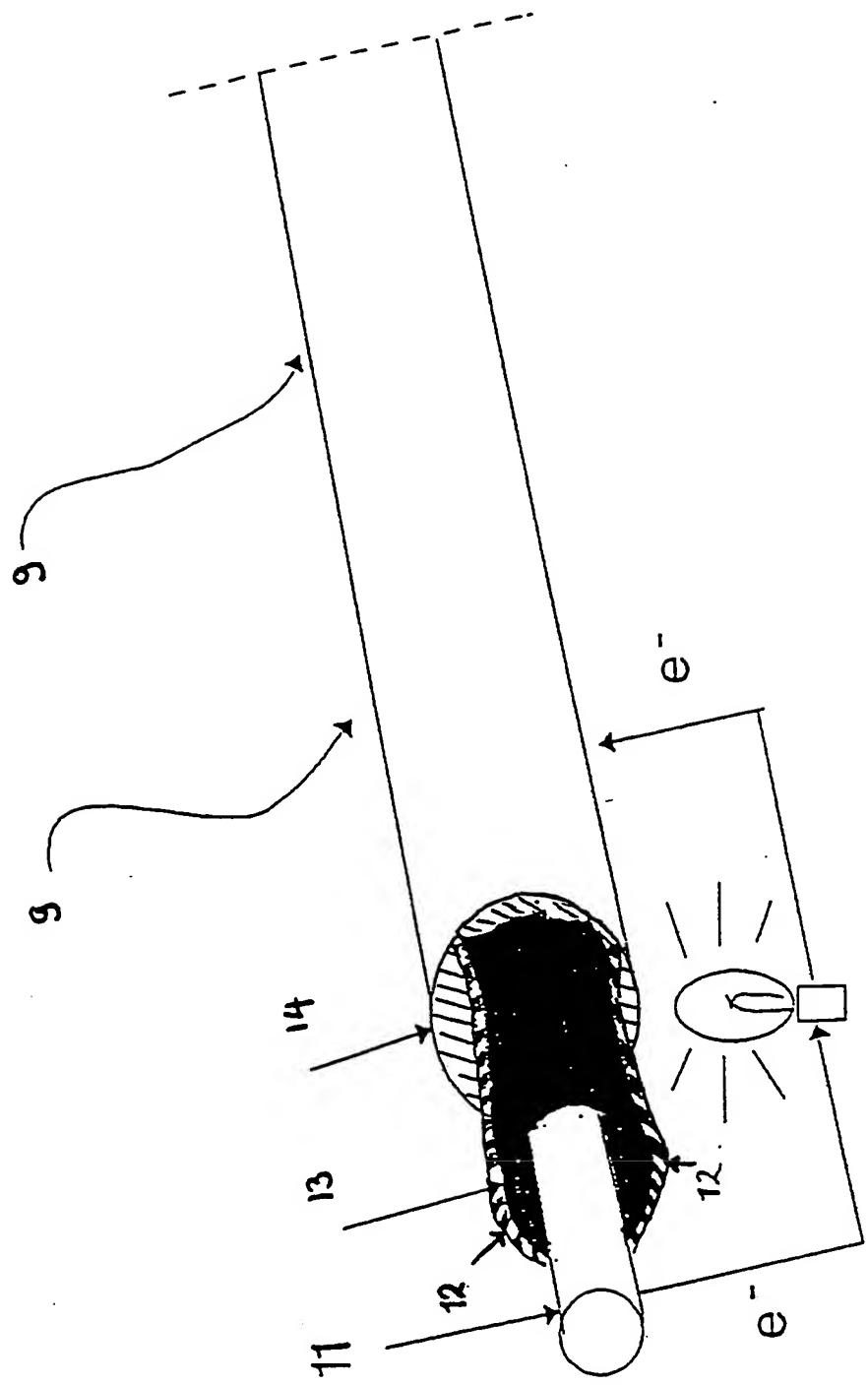


Figure 4



## INTERNATIONAL SEARCH REPORT

PCT/EP 93/00731

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H01G9/20; H01M14/00

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.Cl. 5	H01G ; H01L

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	EP,A,0 333 641 (GEBRÜDER SULZER) 20 September 1989 & US,A,5 084 365 (GRÄTZEL ET AL.) cited in the application	1
A	see the whole document & US,A,4 927 721 (GRÄTZEL ET AL.) cited in the application ---	3,4,7
Y	EP,A,0 046 411 (MATSUSHITA ELECTRIC INDUSTRIAL) 24 February 1982	1
A	see page 6, line 9 - page 9, line 3; figure 1 ---	5,7
A	WO,A,9 116 719 (GRÄTZEL) 31 October 1991 see the whole document ---	1,3,4
		-/-

<sup>10</sup> Special categories of cited documents :<sup>10</sup><sup>"A"</sup> document defining the general state of the art which is not considered to be of particular relevance<sup>"E"</sup> earlier document but published on or after the international filing date<sup>"L"</sup> document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<sup>"O"</sup> document referring to an oral disclosure, use, exhibition or other means<sup>"P"</sup> document published prior to the international filing date but later than the priority date claimed<sup>"T"</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>"X"</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>"Y"</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<sup>"&"</sup> document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

10 JUNE 1993

Date of Mailing of this International Search Report

15.06.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

PUHL A.T.

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 916 035 (YAMASHITA ET AL.) 10 April 1990 see column 4, line 21 - line 37; figure 1 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 179 (E-414)24 June 1986 & JP,A,61 029 179 ( OKI ELECTRIC IND ) 10 February 1986 see abstract ---	2
A	WO,A,8 404 425 (INSTITUT DE MICROTECHNIQUE DE L'UNIVERSITE DE NEUCHATEL) 8 November 1984 see page 3, line 26 - page 4, line 11; figure 1 ---	2
A	US,A,4 476 003 (FRANK ET AL.) 9 October 1984 see the whole document ---	6
A	US,A,5 053 293 (YAMAKITA ET AL.) 1 October 1991 see the whole document -----	1,6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9300731  
SA 71603

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 10/06/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0333641	20-09-89	CH-A-	674596	15-06-90
		JP-A-	1220380	04-09-89
		US-A-	4927721	22-05-90
		US-A-	5084365	28-01-92
-----				
EP-A-0046411	24-02-82	JP-C-	1663229	19-05-92
		JP-B-	3024746	04-04-91
		JP-A-	57138785	27-08-82
		JP-B-	1045712	04-10-89
		JP-C-	1560633	31-05-90
		JP-A-	57038573	03-03-82
		US-A-	4388385	14-06-83
-----				
WO-A-9116719	31-10-91	AU-A-	7748391	11-11-91
		EP-A-	0525070	03-02-93
-----				
US-A-4916035	10-04-90	JP-A-	1315966	20-12-89
		JP-A-	1315967	20-12-89
		JP-A-	1039779	10-02-89
		JP-A-	1124973	17-05-89
		JP-A-	1124974	17-05-89
		JP-A-	1124975	17-05-89
-----				
WO-A-8404425	08-11-84	EP-A-	0140917	15-05-85
-----				
US-A-4476003	09-10-84	None		
-----				
US-A-5053293	01-10-91	JP-A-	3078978	04-04-91
-----				